Bimetallic LDHs origin catalysts containing Co, Fe and Ni for ammonia decomposition to hydrogen and nitrogen

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Significance and Relevance

In the presented studies, bimetallic systems Co-Ni, Fe-Ni and Co-Fe dispersed in MgO/Al_2O_3 matrix were obtained by calcination of layered double hydroxide (LDH) materials. Comparison of N_2-TPD profiles with the results of the catalytic tests showed a synergistic effect between metals leading to a decrease in the temperature of nitrogen molecules desorption and therefore in decreased recombination energy of adsorbed N atoms, which is postulated to be the rate-limiting step in the catalytic decomposition of ammonia to hydrogen.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors. 2nd choice: Sustainable and clean energy production and transport.
Preferred presentation: Poster

Introduction and Motivations

Hydrogen is an environmentally friendly fuel, but for the most purposes its low volumetric energy density in a compressed gas makes its storage and transportation a serious problem. Compared to other potential hydrogen storage materials, ammonia has a high hydrogen storage capacity (17.6% by weight), energy density (3000 Wh/kg) and can be easily liquefied at 20 °C under the pressure of 0.8 MPa. These advantages of ammonia make it promising for hydrogen storage and transportation. Ruthenium-based catalysts for ammonia decomposition showed promising catalytic activities, and a Ru-supported on MgO/CNT and modified with alkali promoters showed the best activity at temperatures below 500 °C. The large-scale use of ruthenium based catalysts may not be feasible due to their high cost and scarcity. Studies on ruthenium catalysts have shown that their good catalytic activity results from the appropriate binding energy of N-metal. Transition metals such as Co, Ni and Fe have been reported to be effective catalysts for ammonia decomposition [1]. The main concept was to use a combination of two metals with nitrogen binding energies lower and higher than ruthenium to potentially mimic the chemical properties of ruthenium. Based on the nitrogen desorption energy, the potential bimetallic systems of Co-Ni, Co-Fe, Fe-Ni were selected for ammonia decomposition [2]. In addition, acidity and basicity of the supports used for deposition of the active metallic phase, play an important role in the customisation of efficient catalytic systems for the ammonia decomposition [3]. The layered double hydroxides (LDHs) offer great opportunities for synthesis of the catalysts with desired properties.

Materials and Methods

Two series of mixed metal oxides derived from layered double hydroxides (LDHs) with bimetallic compositions of transition metals Co-Fe, Co-Ni, and Fe-Ni were prepared as catalyst's precursors. The first series was prepared by direct synthesis of bimetallic system by the coprecipitation method. LDH materials containing Co/Fe/Mg/Al (HCoFe), Co/Ni/Mg/Al (HCoNi), Fe/Ni/Mg/Al (HFeNi) were synthesised. The second series of mixed metal oxides was prepared as follows. First, monometallic systems containing one of the transition metals (TM), such as Co (HCo), Fe (HFe), and Ni (HNi) were synthesised by the coprecipitation method. In the next step, the second metal was deposited on the calcined materials using the incipient wetness impregnation method. The following bimetallic materials: Co-Fe (HCo-iFe), Co-Ni (HCo-iNi), Fe-Co (HFe-iCo), Fe-Ni (HFe-iNi), Ni-Fe (HNi-iFe), and Ni-Co (HNi-iCo) were prepared by this method, where the first metal (in the sample code) denotes the metal introduced during the LDHs synthesis and the second metal (in the sample code) denotes the metal deposited by the incipient wetness impregnation method. All obtained materials were calcined in air at 600 °C for 12 hours and then reduced before the catalytic test at 800 °C in a flow of pure hydrogen. The prepared catalysts were characterised by various methods, including: low-temperature N_2 adsorption-desorption, XRD, H_2-TPR, NH_3-TPD, N_2-TPD, TGA/DSC. The samples obtained were tested as catalysts for ammonia decomposition (dcNH_3) in the temperature range of 250 – 800 °C.

Results and Discussion

Figure 1A shows the results of catalytic tests for bimetallic CoFe, CoNi, and FeNi catalysts obtained from LDH materials, while Figure 2A presents the results of tests for bimetallic catalysts containing Co and Ni obtained by different methods. Figures 1B and 2B show the N_2-TPD results for the corresponding catalysts.

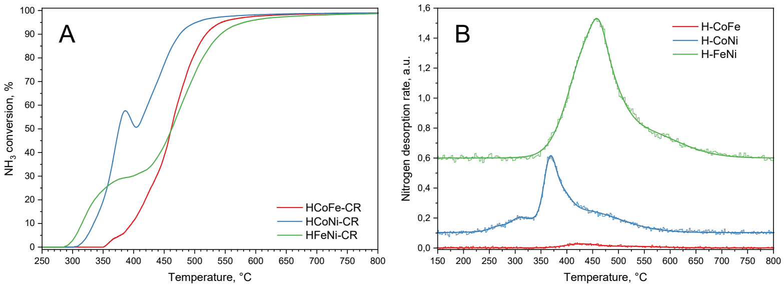

Figure 1. A - Results of catalytic tests for the LDHs-origined bimetallic CoFe, CoNi, FeNi catalysts calcined at 600 °C and then reduced at 800 °C. B - Results of N_2-TPD obtained for the same catalysts.

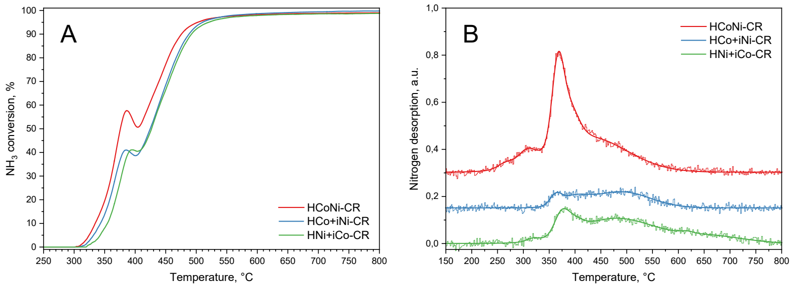

Figure 2. A - Results of catalytic tests for the bimetallic catalyst containing Co and Ni, prepared by different methods, calcined at 600 °C and then reduced at 800°C. B - Results of N_2-TPD for the same catalysts.

In the case of a series of bimetallic catalysts obtained from LDH materials, the best activity was obtained for catalysts containing Ni and Co. Comparison of the ammonia conversion profiles with the nitrogen desorption profiles showed a correlation between the nitrogen desorption temperature and catalytic activity. Nitrogen desorption profile for the HCoNi-CR catalyst begins at 225°C, the lowest temperature compared to the other catalysts, and finished at about 625°C, where the highest level of ammonia conversion was achieved among the catalysts tested in this series. However, the same analysis for the catalysts obtained by different orders of metallic components introduction showed that the HCoNi-CR catalyst (obtained by simultaneous coprecipitation of both metals) resulted in better catalyst than those obtained by depositing of the second metal by impregnation method.

References

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